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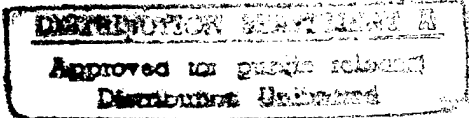
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**13. ABSTRACT (Maximum 200 words)**

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# Cluster Beam Study of Boron Oxide and Hydrogenated Boron Oxide Ion Clusters with Water

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## Abstract

Reactivity of thermalized boron oxide and hydrogenated boron oxide ion clusters in the mass range up to 95 amu, has been studied with water ($D_2O$). Primary reactions are identified, with some information regarding reaction mechanisms as well. The cross section data is converted to surface reaction efficiencies for use in combustion models. The important result in this regard is that the reaction efficiency is low (<1%) and decreases with increasing cluster size, suggesting that water-$B_2O_3$ reactions may not be very important in volatilization. Oxide-water interactions are quite important in determining combustion product distributions. The effects of cluster structure on reactivity is examined and compared with analogous results for reaction with HF. The oxide chemistry is also compared with that for pure boron cluster ions reacting with HF and $D_2O$.

## I. Introduction.

The chemistry of boron oxides with water is critical in two aspects of boron combustion. Boron particles are coated with a passivating oxide layer that must be removed to allow ignition and rapid combustion. Water (and OH) is an important combustion gas produced by oxidation of hydrocarbon components in a typical fuel, propellant, or explosive. If water reactions with the oxide are efficient and result in volatile products, this would enhance combustion by helping to remove the passivating layer. Oxide-water chemistry is also important in determining the final mix of combustion products, and thus, the overall energy release. In particular, it is desirable to avoid production of $(HOBO)_x$ polymers since these have relatively high heats of formation.

This report presents our detailed Cluster Beam results for reaction of small boron oxide cations with water. Deuterated water ($D_2O$) was used to avoid mass interference problems since the $^{10}B$-oxide used in our cluster source has ~6% $^{11}B$ contamination. In previous studies we have found no significant isotope effects on reactivity or product branching[1]. Raw cross sections are presented along with a brief discussion of reaction mechanisms. The cross sections are then converted to surface reaction efficiencies for inclusion in combustion models. Finally, comparisons are made to boron oxide cluster reactions with HF[2,3,4] and with boron cluster reactions with both HF[5,2] and $D_2O$[1].

Boron oxide is highly hygroscopic, and the oxide layer is most likely at least partly converted to a hydrogenated form by interaction with water in the atmosphere or in combustion gases. (We refer to these $B_xO_yH_z$ stoichiometries as hydrogenated oxides, rather than hydroxides, because the bonding arrangement is not entirely clear and may involve some BH as well as OH bonds). In the case of HF, we found that hydrogenation had a profound effect on reactivity of small boron oxide cluster ions[3], therefore this report also covers the analogous reactions with water.

Finally, these results are interesting in light of recent collision-induced dissociation experiments in our lab[6] and an on-going theoretical study[7] of boron oxide cluster structures and energetics. With reasonably certain structures now available for small $B_xO_y^+$ species, we are in a better position to understand what factors control reactivity. Boron oxides thus join boron and carbon as one of the few cluster systems where reliable structure and energetics data are available.

and where detailed chemical studies have been carried out. This combination is important in attempting to understand the nature of cluster bonding and how this controls reactivity.

This report presents both cross section data, relevant to the boron oxide-water reaction mechanism, and surface reaction probabilities. These are suitable for inclusion in boron heterogeneous combustion models[8,9,10].

## II. Experimental Approach.

### *Apparatus.*

All experiments were performed using a guided ion beam mass spectrometer. A detailed description of the apparatus is given elsewhere[11,3,12]. Briefly, boron oxide cluster ions are generated by 12 keV argon atom bombardment of $^{10}B_2O_3$ maintained near its melting point. Complete description of the sample preparation is given in the next section. The hot nascent cluster ions are collected with an rf octapole ion guide and thermalized by a labyrinthine RF trap using 0.01 Torr helium buffer gas.

The desired cluster is selected using a quadrupole filter and then the reactant beam is injected into another octapole ion guide system whose last part is surrounded by a collision cell filled with $D_2O$ vapor ($5 \times 10^{-5}$ Torr). The gas inlet system is heated from the outside to prevent condensation due to supersonic expansion cooling. The neutral target gas pressure is low enough to maintain single-collision conditions. The collision energy can be selected by means of the computer controlled DC voltage between the end of the RF trap and the collision cell octapole. The remaining parent ions and product ions are guided by another octapole, mass analyzed by a second quadrupole and then counted. Relative signal intensities are used to calculate reaction cross sections. Experimental precision and possible errors are discussed elsewhere.

### *Sample Preparation.*

Isotopically purified (94.11 At.% of $^{10}B$) boron oxide ($B_2O_3$) was purchased (Eagle Picher) as a polycrystalline powder. A stainless steel substrate was covered by a thin layer of the loose powder and heated in a furnace at 650°C for about four hours in oxygen environment. A vitreous film of boron oxide can be obtained after reaching at least 450°C and cooling the sample in the natural room conditions. Additional heating (several hours at 350-450°C) in high vacuum

is required due to the hygroscopic nature of boron oxide[13].

## III. Results and discussion.

### Cross Sections.

Direct results of this study are presented as reaction cross sections for all significant product ions, shown in Fig. 1 and Fig. 2 for non-hydrogenated clusters and in Fig. 3 and Fig. 4 for those containing hydrogen. Surface reaction efficiencies calculated from the cross sections are presented in Fig. 5 and Fig. 6 (non-hydrogenated clusters), and in Fig. 7 and Fig. 8 (hydrogenated clusters). Total reactivities and product distributions for all clusters are compared in Fig. 9 (non-hydrogenated) and Fig. 10 (hydrogenated). Fig. 11 compares total reactivity of boron oxide cations toward $D_2O$ and HF.

### A. The system: $B_nO_m^+$ + water.

The dominant reaction and the collision energy dependence of the total reactivity both change dramatically with increasing reactant cluster size and with the reactant stoichiometry. This is very much in contrast to the pattern of reactivity observed for HF, where the same reactions dominated for all reactant sizes and stoichiometry. In addition, the reactivity toward HF is large and shows no signs of activation barriers, while for water is low and suggests large activation barriers for the larger clusters.

For small and oxygen deficient reactant clusters ($BO^+$, $B_2O^+$, and $B_2O_3^+$) the dominant reaction is O-addition:

$$B_nO_m^+ + D_2O \rightarrow B_nO_{m+1}^+ + D_2.$$
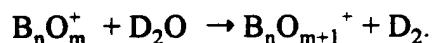
The energy dependence shows that this reaction is exoergic with no activation barrier, but is still only 2-6% efficient, indicating the presence of a bottleneck to reaction. It seems likely that this occurs at the $D_2$ elimination stage.

Another reaction observed for all the small clusters ($BO^+$, $B_2O^+$, $BO_2^+$ and $B_2O_3^+$) is hydroxyl- addition:

$$B_nO_m^+ + D_2O \rightarrow B_nO_{m+1}D^+ + D.$$

Again the reaction is exoergic with no activation energy, but only a few percent efficient. For $BO^+$, $BO_2^+$, and $B_2O_3^+$, D addition is also seen:

$$B_nO_m^+ + D_2O \rightarrow B_nO_mD^+ + OD.$$
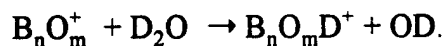
For the larger oxide oligamers, most of the "chemistry" observed is simply fragmentation reactions at collision energies too high to be of any consequence in combustion. For all reactant oxides there is a small reactivity component peaking at low energies, indicating some possibility for reaction with no barrier. The structures of the products are not entirely clear, but most likely are $HO(BO)_n$ or $HO(BO)_nH$ species such as $DB_2O_3$. The efficiency of these reactions is quite small, however, and these are probably not very significant in combustion. In some cases the cross section for a product ion channel will have both low and high energy component. This indicates two different routes to that ion. The low energy mechanisms has to be driven by formation of a stable neutral product, while the high energy component is most likely a simple fragmentation process.

This report will not address the energetics of these reactions, though this is relevant to the thermochemistry of combustion product formation/conversion. We are collaborating with Michael Page and his student Doug Linder on a theoretical/experimental study of boron oxide cluster structures and energetics as this is completed, it will be possible to determine quantitative energetics.

## B. The system: $B_nO_mH^+ + D_2O$.

The effect of hydrogenation was found to be very significant for the boron oxide - hydrogen fluoride system, where all hydrogenated clusters are substantially less reactive.[2,3,4] No dramatic effect is observed in the reactions with water -- possibly because the pure oxide cluster are already quite unreactive. There is a significant decrease of the two major channels for the small clusters: oxygen atom and hydroxyl addition. There are also many new channels observed, however, in many cases these are simply isotope-scrambled analogs. For example,

$$B_2O_3H^+ + D_2O \quad \rightarrow HOBOD^+ + DOBO$$
$$\rightarrow DOBOD^+ + HOBO$$
$$\rightarrow DOBO^+ + HOBOD.$$
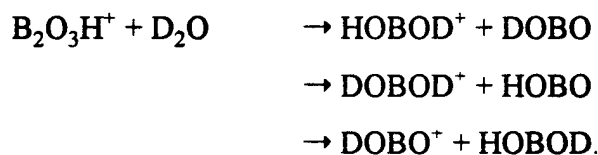
(First three channels shown in the figure -- note, in the figures, we generally write the more complex structures as $B_nO_mH_x$). The fact that these are observed points to a reaction mechanism in which a complex is formed, then decomposes -- similar to the chemisorption/desorption reactions that are expected to dominate for surface chemistry of the oxides.

For the bigger clusters the effects of hydrogenation are more difficult to study. It was impossible to isolate $B_3O_3H^+$ which is only present in a trace amount in the spectrum of boron oxide clusters, and the contamination of the $^{10}B_nO_mH^+$ signal by $^{11}B$-oxide becomes increasingly dominant as the number of boron atoms increases. Even with subtraction of the reaction due to oxides, the cross sections are difficult to extract. For $B_2O_3H^+$ and $B_3O_4H^+$, there is a slight increase in reactivity comparing to the non-hydrogenated species, more pronounced for the latter one. The results may also suggest that $B_2O_3H^+$ is more stable than $B_2O_3^+$ because the threshold for the only dissociation channel observed in the case of the hydrogenated ion seems to be higher than for any dissociation pathway of $B_2O_3^+$.

## C. Comparisons with other systems.

The previous studies[2,3,4] on the system $B_nO_m^+ / B_nO_mH^+$ + HF showed that the dominant reaction channels led to formation of FBO or FBOH:

$$B_nO_m^+ + HF \quad \rightarrow FBOH^+ + B_{n-1}O_{m-1}$$
$$\rightarrow B_{n-1}O_{m-1}^+ + FBOH$$
$$\rightarrow FBO^+ + HB_{n-1}O_{m-1}$$
$$\rightarrow HB_{n-1}O_{m-1}^+ + FBO.$$
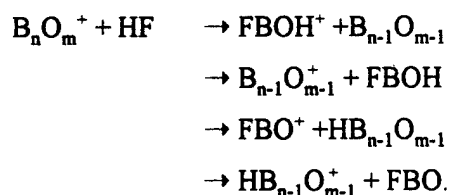
Since HF and water are isoelectronic, one might expect some similarities, and indeed products like HOBOH and HOBO (analogous to FBOH and FBO) are observed for the larger clusters. Reactivity is much lower, however, and no particular product dominate. The reactivity of the two species is compared in Fig. 11.

Results of our collision-induced dissociation experiments[6] show that low reactivity toward water is generally correlated with high cluster stability. The exception is $B_3O_3^+$, which is unreactive despite its low stability.

Reactions of pure boron cluster ions have been studied with both HF[5,14] and $D_2O^{15,1}$. The most important reactions in the two cases are isoelectronic analogs:

$$B_n^+ + D_2O \quad \rightarrow B_{n-1}D^+ + DBO$$
$$B_n^+ + HF \quad \rightarrow B_{n-1}H^+ + BF.$$
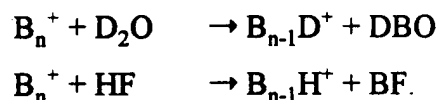
In contrast to the oxides, for pure boron clusters, reaction with water is more efficient than with HF, though both significant.

### D. Reaction efficiencies.

For combustion modeling purposes it is desired to convert reaction cross sections into the equivalent thermal rate parameters. The method of calculating the reaction efficiency has been described elsewhere[14,4]. Briefly speaking, the reaction probability has been estimated by the ratio of the experimentally determined reaction cross section to the collision cross section at the same collisional energy. The collision cross sections are evaluated by the ion - dipole capture cross section at low energy range and by the hard sphere model at high energies. Reaction probabilities $P(E)$ obtained in such a way for a series of data points were subsequently convoluted with the Maxwell-Boltzmann thermal distribution of collision energies. The resulting values $P(T)$ can be used as approximate reaction efficiencies at given temperatures.

The results of such calculations are presented in Fig. 5-8. The efficiencies for all product channels are below 10% and in most of cases even below 1%. The temperature dependence for the oxygen atom addition channel is not consistent through the series of the parent ions. For $BO^+$ the efficiency of $BO_2^+$ formation is increasing over the temperature range taken into account, with a possible saturation or maximum above 3000 K. The reaction of $B_2O^+$ producing $B_2O_2^+$ is almost constant over temperature range between 750 and 3000 K. Formation of $B_2O_3^+$, as the product of $B_2O_2^+$ oxidation, shows a maximum of efficiency between 500 and 1000 K. This maximum is more pronounced for the reaction of the hydrogenated equivalent of this cluster although the maximum of efficiency for this case ($B_2O_3H^+$ formation) lies probably between 1000 and 1500 K. All the above observations would support the assumption of two competing mechanisms leading to the overall addition of the oxygen atom.

For the other reactions the temperature dependences are constant for all reactant clusters. For example, all channels leading to formation of $BO_2D^+$ and $BO_2D_2^+$ show a similar trend of decreasing reaction efficiency with increasing temperature. Generally the total reaction probability shows a tendency to increase with increasing temperature only for $BO^+$. The bigger clusters exhibit an opposite trend with a weak maximum between 500 and 1500 K and for intermediate sizes the temperature dependence is usually not sharply defined. It is important to realize since the reaction efficiency for most of the large clusters comes almost entirely from the small cross section component at low collision energies, these efficiencies are quite suspect. The only clear

conclusion with regard to combustion is that the efficiencies are very low.

## IV. Conclusions.

Reactions in the system $B_nO_m^+ / B_nO_mH^+ + D_2O$ are inefficient, despite at least some channel for reaction with no activation energy. Evidently there are severe bottlenecks inhibiting reaction. The mechanism appears to be analogous to chemisorption/desorption with the product distribution dominated by the most stable species. A single H-atom on the reactant oxide has minimal effect on reactivity.

As our CID results are analyzed together with on-going calculations of Linder and Page, we expect that both the reaction mechanism and some of the thermochemistry will become clear. In particular, we hope to identify the bottleneck for this reaction.

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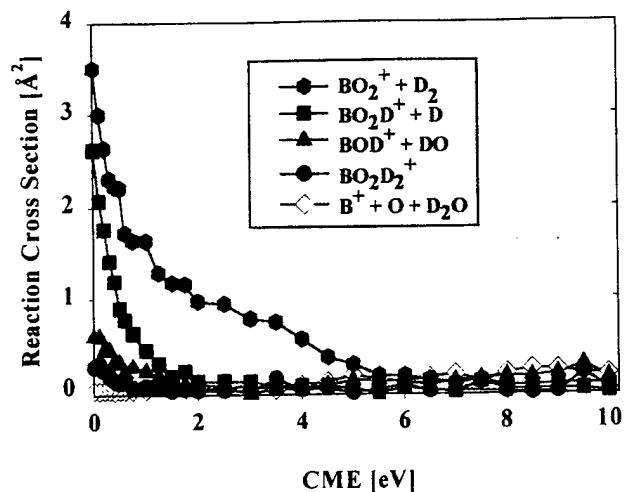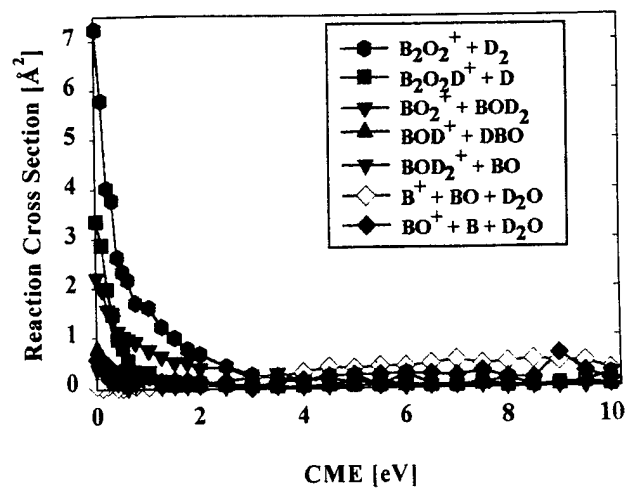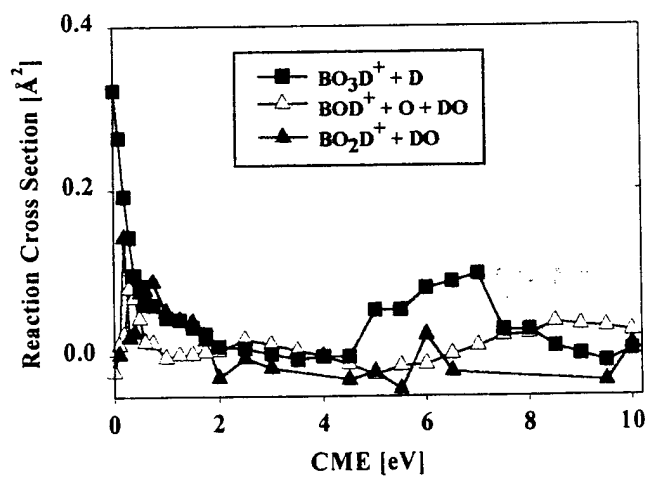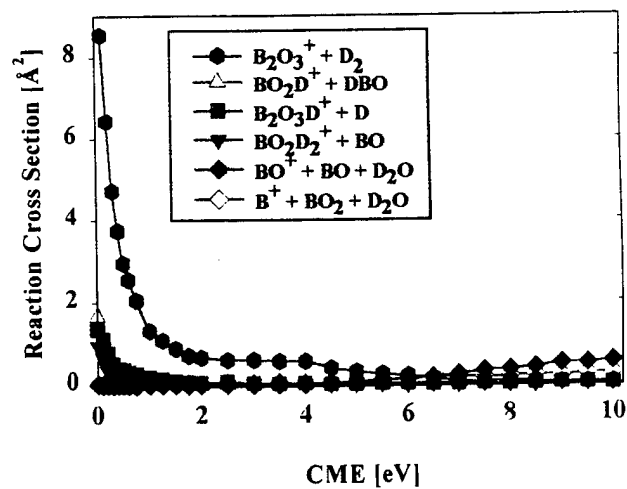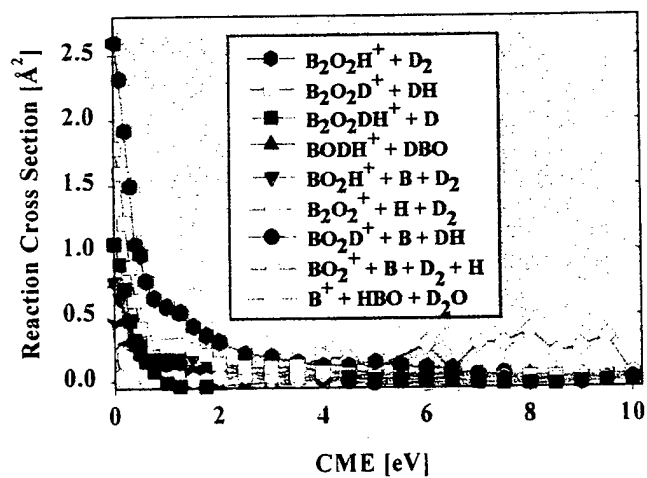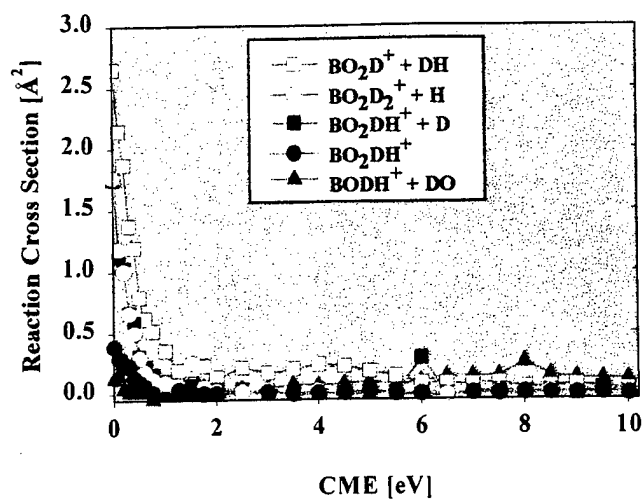
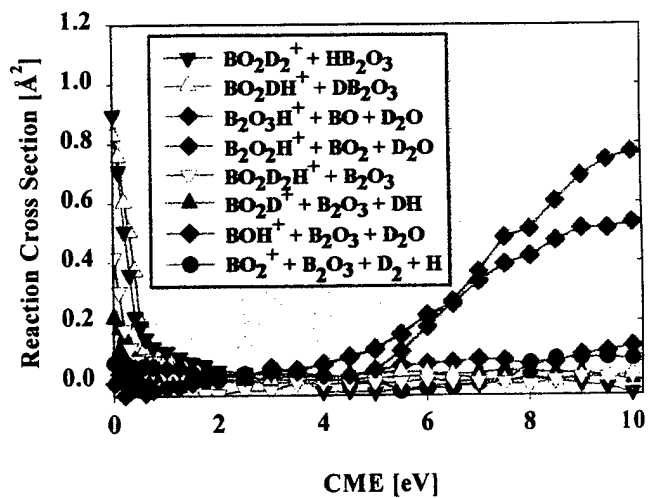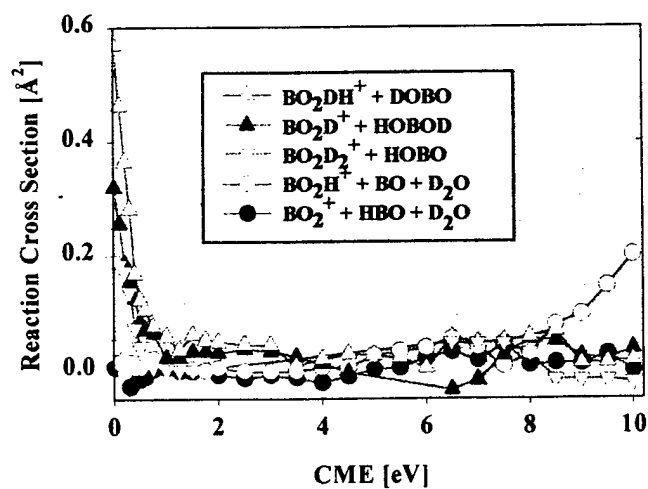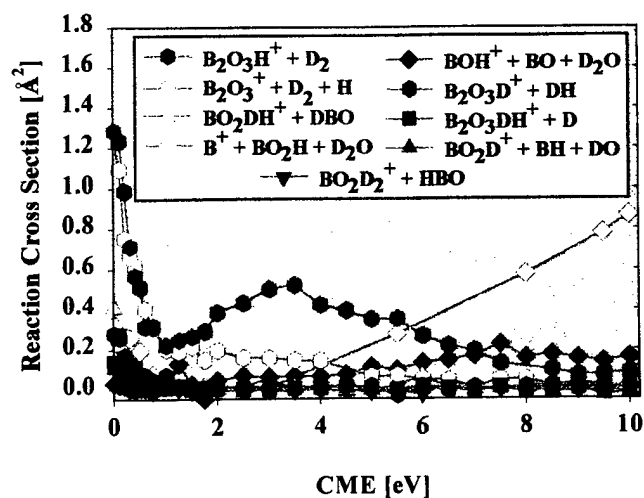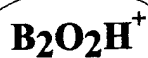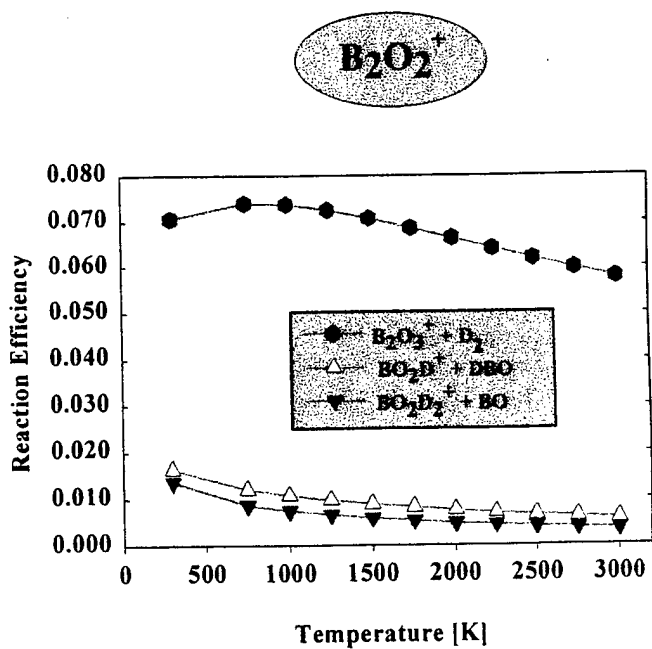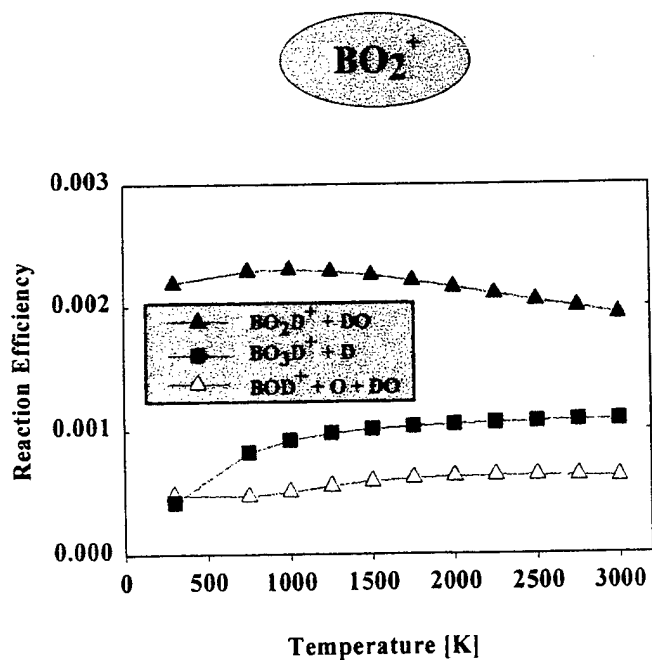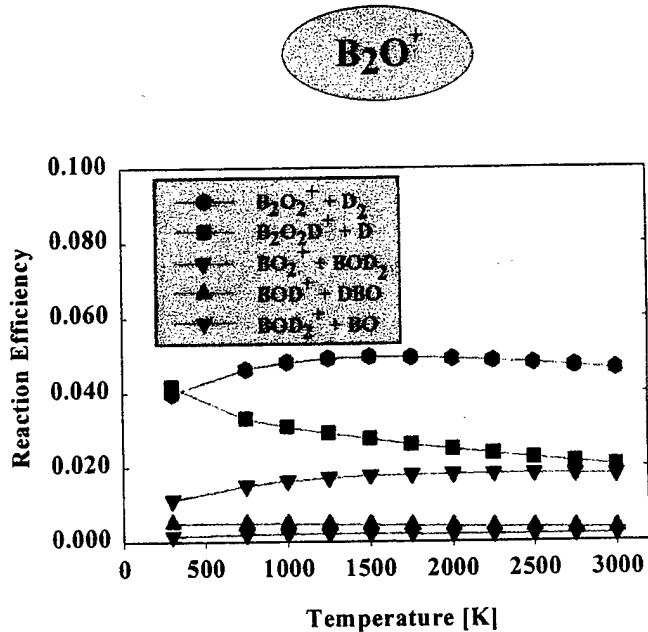Fig. 1. Reaction cross sections for smaller non-hydrogenated clusters.
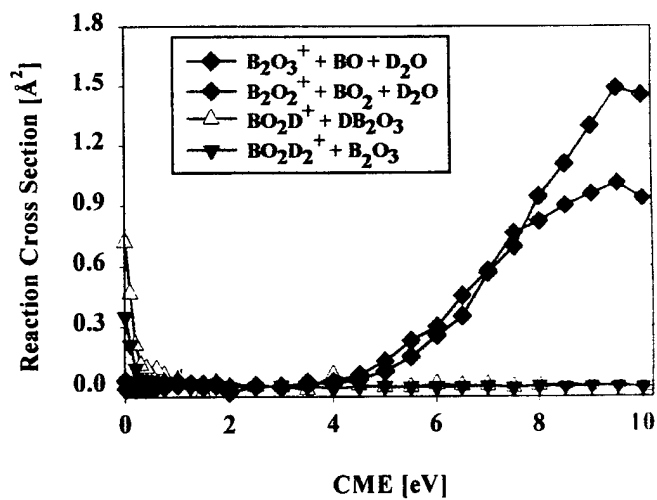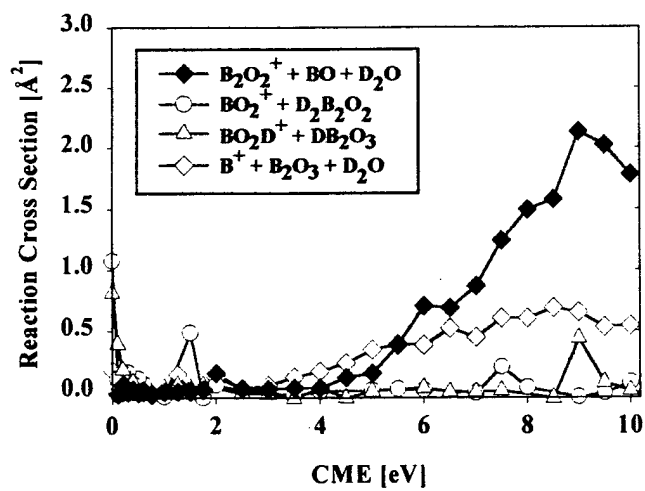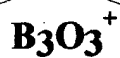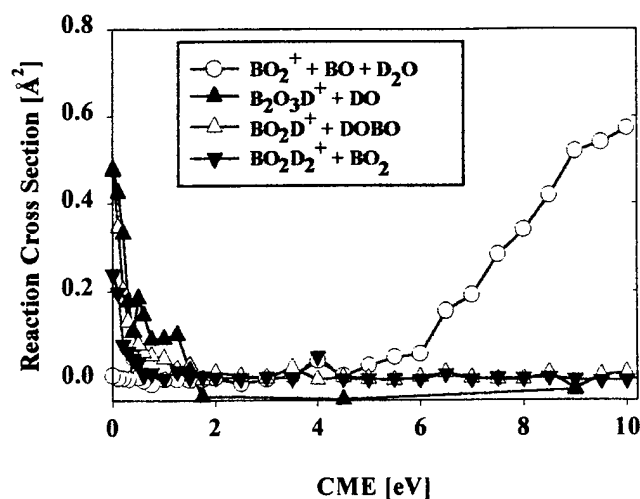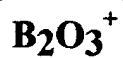
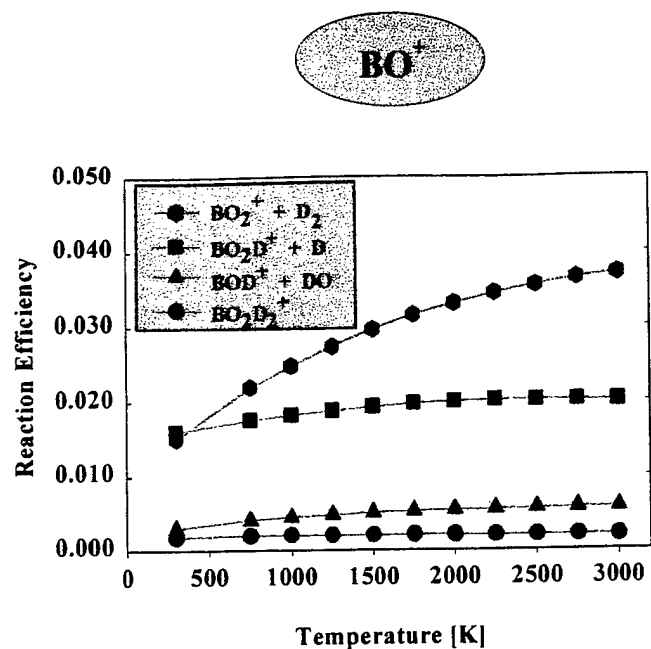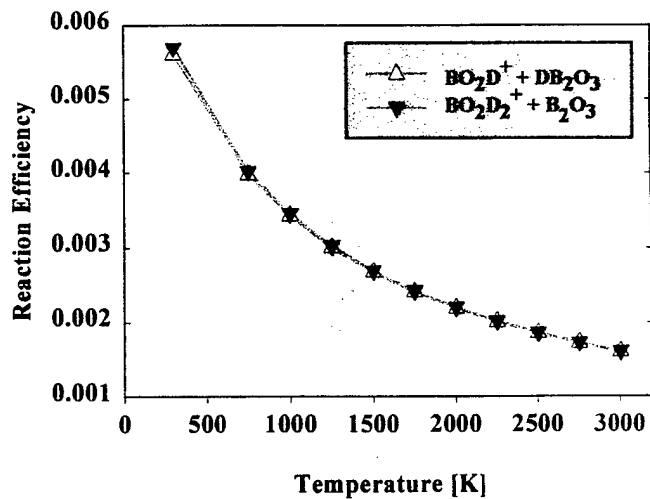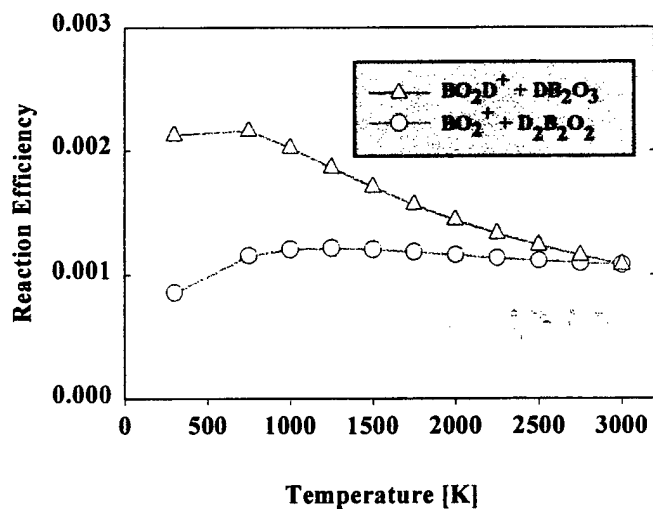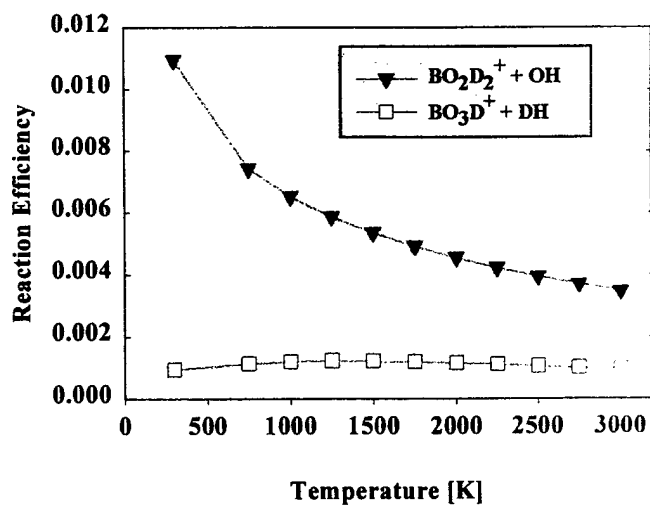Fig. 2. Reaction cross sections for bigger non-hydrogenated clusters.
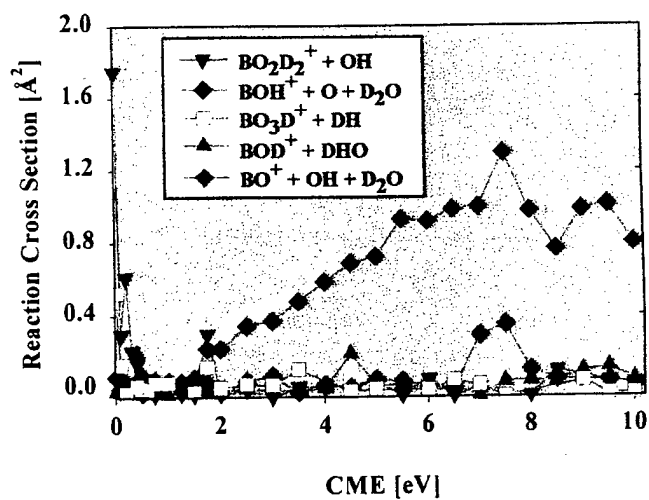
Fig. 3. Reaction cross sections for smaller hydrogenated clusters.

Fig. 4. Reaction cross sections for bigger hydrogenated clusters.

Fig. 5. Reaction efficiencies for smaller non-hydrogenated clusters.
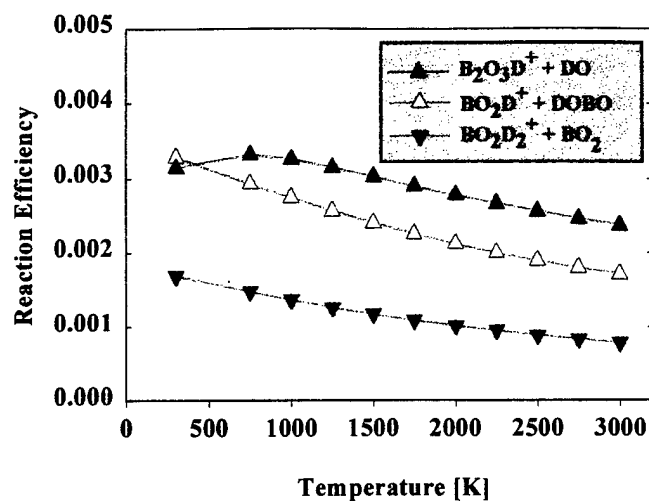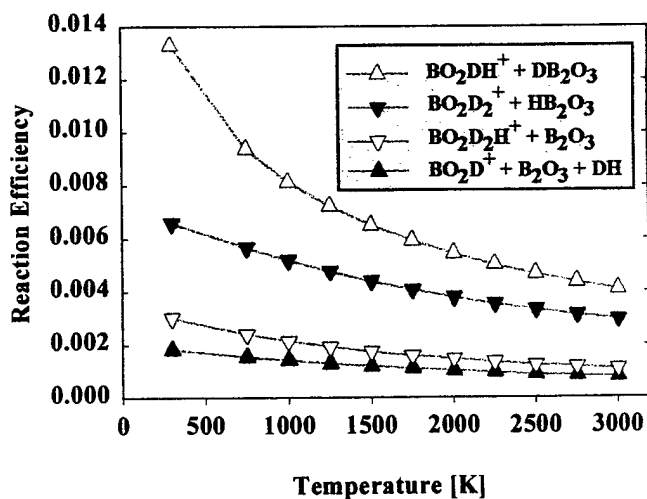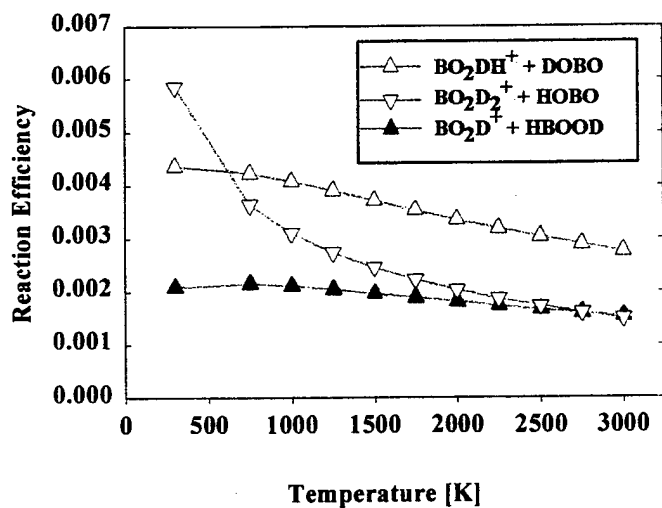
Fig. 6. Reaction efficiencies for bigger non-hydrogenated clusters.
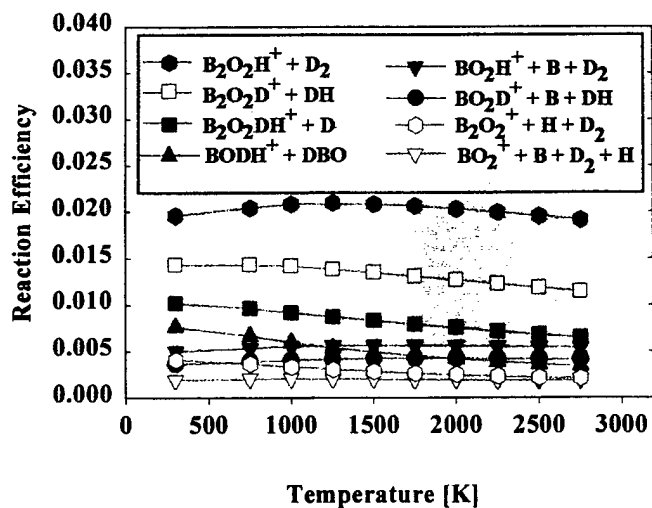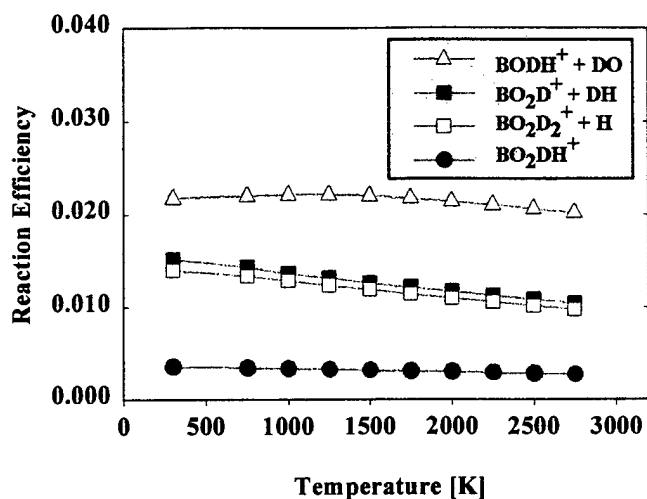
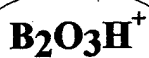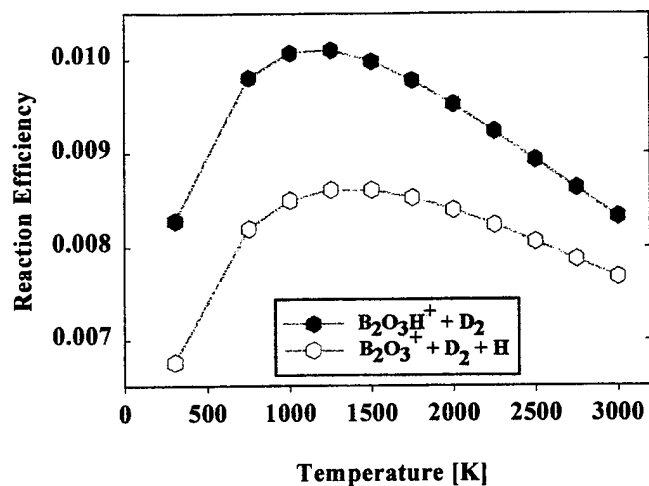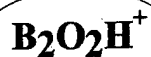Fig. 7. Reaction efficiencies for smaller hydrogenated clusters.

Fig. 8. Reaction efficiencies for bigger hydrogenated clusters.